A 1:2 Complex between 1,4,7,10,13,16-Hexaoxacyclooctadecane (18-Crown-6) and Methyldiphenylsulfonium Di-μ-iodo-bis[diiodomercurate(II)]

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Abstract. $C_{12}H_{24}O_6.2C_{13}H_{13}S^+.Hg_2I_6^{2-}$, $M_r = 1829.55$, monoclinic, $P2_1/c$, $a = 13.144$ (4), $b = 12.157$ (3), $c = 16.475$ (3) Å, $\beta = 95.08$ (2)°, $V = 2622$ Å^3, $Z = 2$, $D_x = 2.32$ g cm^{-3}, $\lambda(Cu\,K\alpha) = 1.54178$ Å, $\mu = 402$ cm^{-1}, $F(000) = 1672$, room temperature, $R = 0.0831$ for 1644 unique observed reflections. The 2:1 complex has a crystallographic centre of symmetry at the centre of the 18-crown-6 ring which adopts the characteristic all-*gauche* conformation with local pseudo D_{3d} symmetry. The two sulfonium cations dock to opposite faces of the macrocycle, each relying upon two C—H···O hydrogen bonds and possibly a weak electrostatic interaction involving the positively charged S atom and a suitably disposed electronegative O atom on the 18-crown-6 ring.

Introduction. Following our recent observation (Allwood, Colquhoun, Crosby, Pears, Stoddart & Williams, 1984) that [Ph₃PMe][PF₆] forms a 2:1 complex with 18-crown-6 (18C6) through C—H···O hydrogen bonding, we decided to examine the ability of alkylsulfonium cations, by virtue of the α-CH acidic groups to bind to 18C6. X-ray crystallographic evidence was obtained (Allwood, Crosby, Pears, Stoddart & Williams, 1984) for both polymeric 1:1 (*e.g.* [PhCH₂SMe₂.18C6]ₙ[PF₆]ₙ and [PhCOCH₂SMe₂.-18C6]ₙ[PF₆]ₙ) and discrete 2:1 (*e.g.* [(PhCOCH-PhSMe₂)₂.18C6][PF₆]₂) complexes. Thus, it appears that, in sulfonium salts carrying two methyl substituents, hydrogen-bond copolymer formation with 18C6 can be interrupted by ensuring that the third substituent group on sulfur is sufficiently large to block the approach by further 18C6 receptors and so direct the supramolecular structure towards a discrete 2:1 complex. Another way to favour these discrete 2:1 complexes is to restrict the number of methyl substituents on sulfur to one. For this reason, we investigated the complexation of [Ph₂SMe][HgI₃] by 18C6. Although the first crystals we isolated (Pears,

Stoddart, Crosby, Allwood & Williams, 1986) corresponded to a 1:1 complex between HgI₂ and 18C6, indicating that [Ph₂SMe][HgI₃] had disproportionated to [Ph₂SMe][I] and HgI₂ under the conditions of the crystal-growing experiment, a second batch of crystals were isolated subsequently and shown to be the sulfur analogue of [(Ph₃PMe)₂.18C6][PF₆]. Here, we describe the X-ray structural analysis of these crystals and identify them as [(Ph₂SMe)₂.18C6][Hg₂I₆].

Experimental. A solution of [Ph₂SMe][HgI₃] in warm MeOH (15 ml) was added to a solution of 18C6 (34 mg) in MeOH (5 ml). The first batch of crystals that were isolated were shown (Pears *et al.*, 1986) by X-ray structural analysis to be a 1:1 complex between HgI₂ and 18C6. Since this was not the expected complex, a more careful inspection of the crystalline mass was carried out. This revealed the presence of other very small and, in general, poorly formed platelets adhering to the walls of the vessel. One of these crystals was removed and used for X-ray analysis. Crystal size 0.05 × 0.18 × 0.25 mm. Refined unit-cell parameters obtained by centring 16 reflections. Nicolet *R*3*m* diffractometer. 2680 independent reflections ($\theta \le 50°$) measured, Cu *K*α radiation (graphite monochromator), ω scan; 1644 [$|F_o| > 3\sigma(|F_o|)$] considered observed, index range $h -13/13$, $k\,0/12$, $l\,0/16$; two check reflections measured every 50 reflections, net count constant; data brought to uniform scale, Lorentz and polarization corrections, empirical absorption correction for a lamellar crystal based upon 299 azimuthal measurements, maximum and minimum transmission factors 0.35 and 0.05, respectively (the maximum value is higher than the estimated value of 0.14 that would be expected for the measured thickness of the crystal, the dimension which is most likely to be in error). There was no undue diffuseness of the diffraction peaks. Structure solved by heavy-atom method; non-H atoms refined anisotropically. Phenyl groups refined as

Table 1. *Atom coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($\text{Å}^2 \times 10^3$) *with e.s.d.'s in parentheses*

	x	y	z	U_{eq}*
O(1)	5202 (16)	6175 (20)	1520 (13)	79 (9)
C(2)	5371 (23)	7320 (31)	1389 (21)	75 (14)
C(3)	4527 (25)	7633 (33)	846 (22)	97 (16)
O(4)	4561 (16)	7212 (17)	35 (12)	65 (8)
C(5)	3862 (31)	7634 (33)	−564 (25)	107 (19)
C(6)	4117 (33)	7083 (27)	−1410 (22)	100 (16)
O(7)	3955 (19)	6029 (18)	−1357 (12)	82 (9)
C(8)	4123 (24)	5457 (31)	−2119 (21)	84 (15)
C(9)	3962 (26)	4290 (28)	−2062 (18)	76 (13)
S(1)	2816 (6)	5200 (7)	572 (4)	59 (3)
C(10)	3844 (18)	4372 (26)	291 (18)	55 (11)
C(11)	1639 (16)	3822 (15)	−435 (14)	71 (14)
C(12)	871 (16)	3646 (15)	−1062 (14)	96 (18)
C(13)	285 (16)	4527 (15)	−1381 (14)	105 (20)
C(14)	466 (16)	5584 (15)	−1073 (14)	99 (19)
C(15)	1233 (16)	5760 (15)	−445 (14)	84 (16)
C(16)	1819 (16)	4879 (15)	−127 (14)	46 (10)
C(17)	2123 (18)	3585 (16)	1569 (9)	88 (16)
C(18)	1925 (18)	3218 (16)	2341 (9)	95 (16)
C(19)	2141 (18)	3894 (16)	3019 (9)	82 (16)
C(20)	2556 (18)	4938 (16)	2923 (9)	104 (19)
C(21)	2755 (18)	5305 (16)	2151 (9)	81 (15)
C(22)	2538 (18)	4628 (16)	1473 (9)	56 (11)
Hg	1355 (1)	5288 (1)	5659 (1)	96 (1)
I(1)	3066 (2)	4136 (2)	5391 (1)	70 (1)
I(2)	340 (2)	6191 (2)	4138 (2)	86 (1)
I(3)	1482 (2)	6858 (3)	6803 (2)	109 (1)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Bond lengths* (Å), *bond angles* (°) *and torsional angles* (°)

O(1)—C(2)	1·430 (44)	O(1)—C(9′)	1·466 (38)
C(2)—C(3)	1·415 (45)	C(3)—O(4)	1·435 (41)
O(4)—C(5)	1·386 (44)	C(5)—C(6)	1·608 (56)
C(6)—O(7)	1·304 (40)	O(7)—C(8)	1·469 (41)
C(8)—C(9)	1·439 (51)	C(9)—O(1′)	1·466 (38)
S(1)—C(10)	1·778 (29)	S(1)—C(16)	1·710 (22)
S(1)—C(22)	1·709 (19)	Hg—I(1)	2·718 (3)
Hg—I(2)	2·944 (3)	Hg—I(3)	2·677 (4)
Hg—I(2′)	2·906 (3)	I(2)—Hg′	2·906 (3)
C(2)—O(1)—C(9′)	110·4 (23)	O(1)—C(2)—C(3)	103·5 (27)
C(2)—C(3)—O(4)	113·9 (29)	C(3)—O(4)—C(5)	117·2 (27)
O(4)—C(5)—C(6)	106·7 (30)	C(5)—C(6)—O(7)	107·7 (30)
C(6)—O(7)—C(8)	111·7 (27)	O(7)—C(8)—C(9)	112·2 (28)
C(8)—C(9)—O(1′)	108·2 (26)	C(10)—S(1)—C(16)	104·5 (12)
C(10)—S(1)—C(22)	102·8 (13)	C(16)—S(1)—C(22)	106·4 (11)
S(1)—C(16)—C(15)	116·3 (7)	S(1)—C(16)—C(11)	123·4 (7)
S(1)—C(22)—C(21)	114·3 (7)	S(1)—C(22)—C(17)	125·7 (7)
I(1)—Hg—I(2)	111·9 (1)	I(1)—Hg—I(3)	118·7 (1)
I(2)—Hg—I(3)	109·2 (1)	I(1)—Hg—I(2′)	110·7 (1)
I(2)—Hg—I(2′)	92·0 (1)	I(3)—Hg—I(2′)	111·2 (1)
Hg—I(2)—Hg′	88·0 (1)		
O(1)—C(2)—C(3)—O(4)	−71 (4)	C(6)—O(7)—C(8)—C(9)	179 (3)
C(2)—C(3)—O(4)—C(5)	−169 (3)	O(7)—C(8)—C(9)—O(1′)	−70 (3)
C(3)—O(4)—C(5)—C(6)	176 (3)	C(8)—C(9)—O(1′)—C(2′)	175 (3)
O(4)—C(5)—C(6)—O(7)	64 (4)	C(9)—O(1′)—C(2′)—C(3′)	−178 (3)
C(5)—C(6)—O(7)—C(8)	177 (3)		

idealized rigid bodies (C—C = 1·395 Å); positions of phenyl and methylene H atoms calculated (C—H = 0·96 Å), assigned isotropic thermal parameters, $U(\text{H}) = 1·2 \ U_{eq}(\text{C})$, allowed to ride on parent C atoms. H atoms of methyl groups could not be located unambiguously in ΔF map. Refinement using F magnitudes by block-cascade full-matrix least squares; $R = 0·083$; $wR = 0·086$ [$w^{-1} = \sigma^2(F) + 0·002F^2$]; $(\Delta/\sigma)_{max} = 0·005$; residual electron density in difference map within $-1·17$ and $+1·34$ e Å⁻³; the poor final value for R is probably partly a result of the poor crystal quality and irregular shape coupled with the high value of μ as well as the consequent errors associated with having to rely upon an empirical absorption correction; atomic scattering factors and dispersion corrections from *International Tables for X-ray Crystallography* (1974). Computations carried out on an Eclipse S140 computer using *SHELXTL* program system (Sheldrick, 1983).

Discussion. Table 1* lists the fractional atomic coordinates of the non-H atoms, Table 2 the bond lengths and angles, and selected torsional angles.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters, and a figure showing the view of the 2:1 complex normal to the mean plane of the six macrocyclic O atoms have been deposited with the British Library Lending Divison as Supplementary Publication No. SUP 42723 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
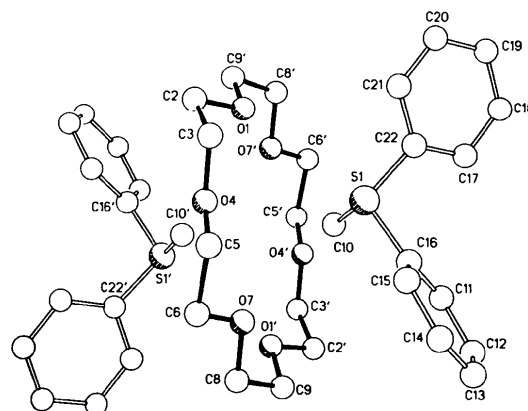

Fig. 1. The supramolecular structure of $[(\text{Ph}_2\text{SMe})_2.18\text{C6}]^{2+}$ with the atomic-numbering scheme.
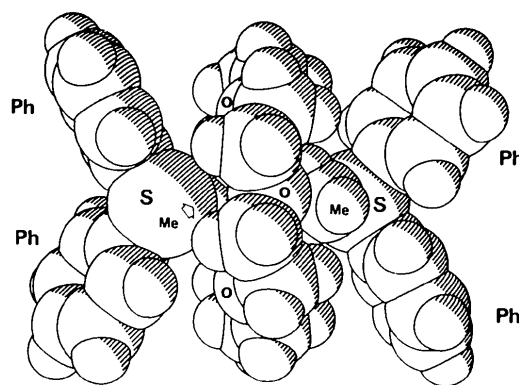

Fig. 2. Space-filling representation of $[(\text{Ph}_2\text{SMe})_2.18\text{C6}]^{2+}$. The methyl H atoms correspond to calculated positions.

The structure of the $[(Ph_2SMe)_2.18C6]^{2+}$ component of the 2:1 complex is illustrated in Fig. 1 which includes the atomic-numbering scheme. Fig. 2 shows a space-filling representation of the 2:1 complex corresponding closely to the skeletal view illustrated in Fig. 1, although the positions of the methyl H atoms were not determined: they have been incorporated assuming normal staggered geometries about the $S-CH_3$ bonds.

There is a crystallographic centre of symmetry at the centre of the 18C6 ring which adopts a characteristic all-*gauche* conformation with local pseudo D_{3d} symmetry. The two sulfonium cations approach opposite faces of the macrocycle with the two methyl groups lying on an axis approximately normal ($9°$ to the normal) to the mean plane of the six macrocyclic O atoms: the $S-CH_3$ bonds are inclined at $39°$ to this plane. This geometry of approach of guest to host is very similar to that observed (Allwood, Crosby, Pears, Stoddart & Williams, 1984) in the structure of $[(PhCOCHPhSMe_2)_2.18C6][PF_6]_2$.

The absence of experimental H-atom positions for the two methyl groups precludes detailed discussion of any hydrogen-bonding interactions. We would expect that the steeply inclined approach of the $S-CH_3$ bonds relative to the mean plane of the macrocycle would result ideally in a two-point $C-H\cdots O$ hydrogen bonding between each methyl group and four of the ether O atoms as observed (Allwood, Crosby, Pears, Stoddart & Williams, 1984) in the structure $[(PhCO-CHPhSMe_2)_2.18C6][PF_6]_2$. Indeed, this is so. The shortest $C(10)\cdots O$ distances in the structure of $[(Ph_2SMe)_2.18C6][Hg_2I_6]$ are 2·93 (1) and 3·29 (1) Å to $O(4')$ and $O(7')$, respectively. The methyl atom is displaced 1·78 (2) Å from the mean plane of the six O atoms in the macrocycle and the through-the-ring $Me\cdots Me$ distance is 3·61 (5) Å.

An interesting consequence of the tilted approach of the $S-CH_3$ bonds to the plane of the macrocycle is a fairly close approach [3·52 (2) Å] of S(1) to O(4) [also S(1') to O(4')]. This could be construed as indicating a weak electrostatic interaction between the S atoms which carry formal positive charges and the electronegative O atoms.

The 18C6 molecules are positioned about the crystallographic centres of symmetry at $(\frac{1}{2}, \frac{1}{2}, 0)$ and $(\frac{1}{2}, 0, \frac{1}{2})$.

There are no short intermolecular contacts between the 2:1 complexes and the $[Hg_2I_6]^{2-}$ counterions, which are positioned about the crystallographic centres of symmetry at (0, 0, 0) and $(0, \frac{1}{2}, \frac{1}{2})$. The geometry of the $Hg_2I_6^{2-}$ counterion is similar to those reported (Contreras, Seguel & Hönle, 1980; Beurskens, Bosman & Cras, 1972) for the tetrapropylammonium and 1,2,4-trithiolane-3,5-bis(N,N-diethyliminium) di-μ-iodo-bis-[diiodomercurate(II)] salts.

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Structure and EXAFS of Diaquatetrakis(imidazole)cobalt(II) Dichloride

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Abstract. $[Co(C_3H_4N_2)_4(H_2O)_2]Cl_2$, $M_r=438·18$, monoclinic, $C2/c$, $a = 12·419$ (2), $b = 11·018$ (2), $c = 15·865$ (3) Å, $\beta = 120·66$ (1)°, $V = 1867·6$ (5) Å^3, $Z = 4$, D_m(flotation, CCl_4/cyclohexane mixture) = 1·553, $D_x = 1·559$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 11·82$ cm^{-1}, $T = 295$ K, $F(000) = 900$, final $R = 0·044$